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Methods Matter: Methods for Sampling Microplastic and Other Anthropogenic Particles and Their Implications for Monitoring and Ecological Risk Assessment

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ABSTRACT

To inform mitigation strategies and understand how microplastics affect wildlife, research is focused on understanding the sources, pathways, and occurrence of microplastics in the environment and in wildlife. Microplastics research entails counting and characterizing microplastics in nature, which is a labor-intensive process, particularly given the range of particle sizes and morphologies present within this diverse class of contaminants. Thus, it is crucial to determine appropriate sampling methods that best capture the types and quantities of microplastics relevant to inform the questions and objectives at hand. It is also critical to follow protocols with strict quality assurance and quality control (QA/QC) measures so that results reflect accurate estimates of microplastic contamination. Here, we assess different sampling procedures and QA/QC strategies to inform best practices for future environmental monitoring and assessments of exposure. We compare microplastic abundance and characteristics in surface-water samples collected using different methods (i.e., manta and bulk water) at the same sites, as well as duplicate samples for each method taken at the same site and approximate time. Samples were collected from 9 sampling sites within San Francisco Bay, California, USA, using 3 different sampling methods: 1) manta trawl (manta), 2) 1-L grab (grab), and 3) 10-L bulk water filtered in situ (pump). Bulk water sampling methods (both grab and pump) captured more microplastics within the smaller size range (<335 µm), most of which were fibers. Manta samples captured a greater diversity of morphologies but underestimated smaller-sized particles. Inspection of pump samples revealed high numbers of particles from procedural contamination, stressing the need for robust QA/QC, including sampling and analyzing laboratory blanks, field blanks, and duplicates. Choosing the appropriate sampling method, combined with rigorous, standardized QA/QC practices, is essential for the future of microplastics research in marine and freshwater ecosystems. *Integr Environ Assess Manag* 2021;17:282–291. © 2020 SETAC

Keywords: Microplastics   Sampling methods   Monitoring   Quality assurance and quality control   Exposure assessment

INTRODUCTION

Ubiquitous microplastic pollution (plastic particles <5 mm in size) in aquatic ecosystems is a growing concern globally, with future concentrations predicted to increase by an order of magnitude by 2025 (Jambeck et al. 2015). To help inform mitigation strategies and understand how microplastics may affect wildlife, research is focused on understanding the sources, pathways, and occurrence in the environment and in wildlife.

Microplastics are widespread in freshwater and marine ecosystems and can be found from the surface water to the deep sea (Thompson 2015). Microplastics are diverse, and they include many morphologies, sizes, colors, and polymer types (Rochman et al. 2019). This diversity is a result of the many plastic products used in society that enter the environment from a myriad of pathways, including agricultural and urban runoff and effluent discharge from wastewater treatment plants (Cole et al. 2011; Sutton et al. 2019). Microplastics are generally classified as primary microplastics (i.e., manufactured and released in their original form) or secondary microplastics (i.e., formed as a result of the breakdown of large plastic debris) (Cole et al. 2011; Rochman et al. 2016). An example of a primary microplastic is a microbead added as an abrasive in facewash, and an example of a secondary microplastic is a fragment derived from the weathering of a plastic bottle cap. The size, morphology, and polymer type of microplastics in environmental samples can help inform identification of the potential sources to aquatic ecosystems (Helm 2017).

Not only are microplastics ubiquitous in the environment, but they are also ubiquitous in animals (Chae and An 2017). Exposure to microplastics can be hazardous to aquatic animals. Microplastic uptake can cause physical effects

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(Wright et al. 2013), which can vary by size or morphology (Bucci et al. 2020), and/or chemical effects due to the chemicals added during manufacturing or via their capacity to sorb toxic chemicals from ambient water (Rochman et al. 2016). Understanding the concentrations of microplastics in nature and their characteristics can help inform whether they may cause an adverse impact to wildlife in a risk assessment framework.

To inform effective management strategies, we must develop an understanding of the environmental occurrence of microplastics that is relevant to the management questions and study objectives. For example, to evaluate whether legislative measures such as a microbead ban are reducing microplastics in the environment, we must collect and characterize samples in a manner that would capture a representative assortment of particles in a size range that would include microbeads. Moreover, to understand risks to wildlife, we must be able to measure microplastic exposure with an accurate quantification of the size, type, and abundance of microplastics that are relevant to the species of interest. For example, manta trawls with a mesh size of approximately 0.3 mm are designed to capture larger floating particles and therefore may be more relevant for the assessment of organisms that feed on particles greater than 0.3 mm. Conversely, bulk water sampling methods capture much smaller particles (Barrows et al. 2017), which smaller planktonic organisms are more likely to ingest.

Currently, there are no standardized sampling methods and protocols for quantifying microplastics across different environmental matrices (Hermsen et al. 2018). Therefore, whether we are sampling surface water or the sea floor, we need to assess the available methods and their limitations (GESAMP 2015, 2019; Hanvey et al. 2017). It is crucial to determine an appropriate sampling method that captures an accurate estimate of microplastic particles most relevant to the questions and objectives at hand.

Equally important, it is critical that robust quality assurance and quality control (QA/QC) measures are implemented with the sampling method so that the accuracy of the results can be evaluated. These QA/QC measures should include accounting for procedural contamination by collecting field and laboratory blanks to avoid overestimation of microplastics (Hanvey et al. 2017). Although background contamination of field samples has always been a concern in microplastics research, to date few studies employ field blank samples (Barrows et al. 2017). In addition, it is important to assess method precision using duplicate samples that measure variability associated with collection, extraction, and analyses. Including strong QA/QC practices will allow for robust monitoring and assessments of microplastics exposure.

An outgrowth of a larger research project to assess the spatial distribution of microplastics in the San Francisco Bay (SF Bay), California, USA, and the 3 adjacent National Marine Sanctuaries (NMSs; Sedlak et al. 2017; Sutton et al. 2019), the present article focuses on lessons learned by closely assessing one of many sample matrices collected in SF Bay: surface water. We use this exercise as a case study to evaluate sampling strategies and determine best QA/QC practices to inform future environmental monitoring programs for microplastics and other anthropogenic microparticles (hereinafter referred to as "microparticles"). We compare microparticle abundance, size, and morphology among different surface-water samples collected using different methods (i.e., manta and bulk water) and among duplicate samples using the same collection methods taken at the same sampling site and time. Overall, our objective is to inform best practices for microplastics research aimed at designing studies that are relevant to the research and management questions, including to inform mitigation strategies or ecological risk assessment.

METHODS

Sample location

The SF Bay is the largest estuary on the west coast of the Americas. For more than 25 y, the Regional Monitoring Program for Water Quality in SF Bay (RMP) has been monitoring SF Bay for basic water quality parameters (e.g., pH, nutrients), legacy pollutants, and emerging contaminants, which now includes microplastics, to provide information to policy makers, stakeholders, and regulators (SFEI 2017). San Francisco Bay is surrounded by densely populated urban areas and receives the majority of its inflow from the San Joaquin and Sacramento rivers, which enter the estuary to the north. Approximately 40% of the state of California drains into SF Bay and Delta. San Francisco Bay discharges surface water through the Golden Gate to the Pacific Ocean, where there are 3 NMSs that were included in the present study (i.e., Greater Farallones, Cordell Bank, and Monterey Bay).

Sample collection

In the present study, we used a subset of samples collected as part of the larger baseline monitoring assessment of microplastics in the SF Bay and NMSs (Sedlak et al. 2017). Samples for the present study were selected from 9 sampling sites (1 sample per site; $n = 1$) that were distributed throughout SF Bay and NMSs and where all 3 methodologies were used (Figure 1). At each site, microparticles were collected using 3 different sampling methods: 1) manta trawl (manta), 2) 1-L grab (grab), and 3) bulk water filtered in situ (pump). The latter two are bulk water sampling methods, but sample different volumes and employ different filtering methods (i.e., in the laboratory versus in situ). To allow for more accurate comparison among sample types, samples at each site were taken on the same day and at roughly the same time.

Manta samples were collected by towing a manta trawl net with a rectangular opening of 16 cm high × 61 cm wide, and a 3-m long, 30 × 10 cm^2, 335-μm mesh. The manta net deployed at the surface for a 30-minute trawl at each site, maintaining tow speeds below 3 knots while the vessel maintained a consistent heading. If there was a current, sample collection was conducted against the current (i.e.,

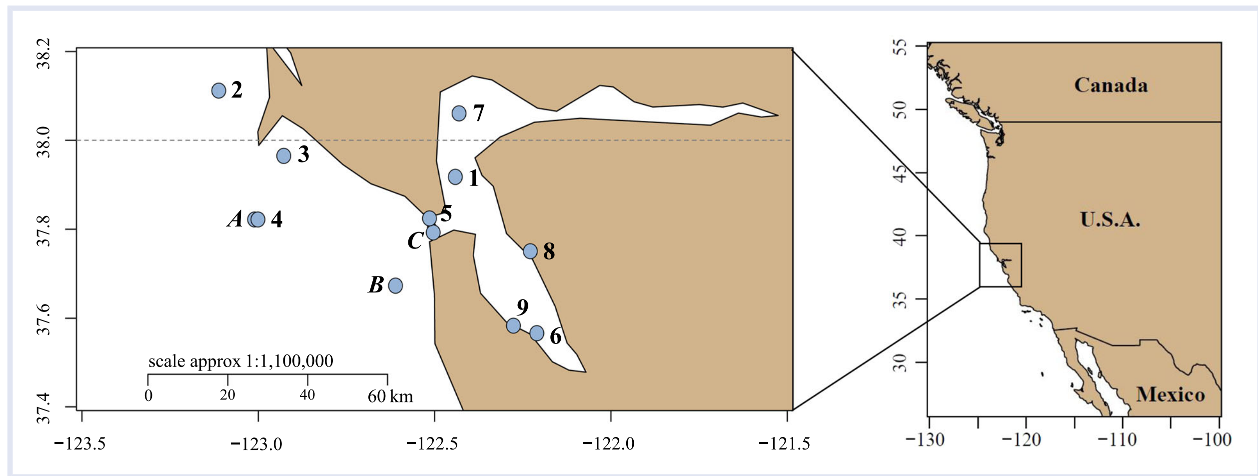

Figure 1. Representation of sampling sites in the San Francisco Bay and adjacent National Marine Sanctuaries in California, USA. Field samples were collected from stations 1 through 9. Samples collected from stations A, B, and C include field duplicates for QA/QC. The *y*-axis denotes latitude values and the *x*-axis denotes longitude values.

the vessel was pointed into the current). After deployment, the manta net was brought on board and rinsed from the exterior to flush materials toward the cod end of the trawl. The cod end, held in place by 2 marine-grade stainless steel hose clamps, was separated from the net and all material captured in the cod end was rinsed onto a 355-µm sieve with deionized water (DI). The contents of the sieve were then rinsed with DI water into a precleaned 500-mL glass sample jar (semi-volatile organic analysis cleaned, Environmental Sampling Supplies [ESS], San Leandro, CA). A clean metal spoon and clean metal tweezers were used to transfer recalcitrant material remaining on the sieve to the sample jar. To prevent bacterial and algal growth, 70% isopropyl rubbing alcohol was added to each sample jar (enough to represent about 10% of the liquid in the jar). All sample jars were placed in coolers containing ice and then were transferred to the San Francisco Estuary Institute (SFEI), where they were stored in a refrigerator at 2 °C prior to being shipped to the University of Toronto, Canada, for analysis.

Two field blanks (1 collected in the bay and 1 in the NMS) were collected during manta trawl sampling to evaluate field procedural contamination. In addition, to measure site-specific sample variability using manta (sites A and C) and grab sampling (sites A and B), field duplicates ($n = 2$; both collected in the NMSs) were collected to assess the precision of the sampling event. Field blanks were collected by pouring 2 L of DI water through the manta trawl, followed by the same field processing procedures used for field samples. The cod end was removed and rinsed into a 355-µm sieve and all contents were rinsed into a sample jar. Field duplicates for the manta trawl were collected by returning to the original site location and resampling along the same trajectory as the primary sample, using the original coordinates, heading, speed, and duration.

One-liter grab samples were collected by filling a 1-L precleaned amber glass wide-mouth bottle (ESS, San Leandro, CA) with surface water prior to collecting the manta trawl sample. The bottle was attached to a 2-m pole to submerge and fill the sample container with undisturbed surface water alongside the research vessel. Prior to collecting the sample, the bottle was rinsed with surface water 3 times by placing the bottle below the surface to fill it, capping the bottle and shaking the bottle before discarding the water. After rinsing 3 times, the field sample was collected and placed in a cooler with wet ice. The sample was transported back to SFEI where it was maintained in a refrigerator at 2 °C prior to being shipped to the University of Toronto for analysis.

Two 1-L grab sample field blanks were collected by filling sample containers with DI water on the vessel just after a field sample was collected, using the same techniques. Field blanks were placed on ice in coolers with the primary field samples and transported sent back to SFEI with the primary field samples. Field duplicates were also sampled and collected immediately after the primary sample using the same techniques.

To evaluate an additional collection method for smaller microparticle size fractions, a pump-filtration system was designed to collect particles 20 µm and larger (Sedlak et al. 2017). Four to 10 L of surface water from each site were pumped through a 20-µm polycarbonate (PC) filter for analysis using a stainless steel bucket to collect a surface-water grab. The variation in water volume sampled was due to the variation of particulate inorganic and organic matter at each site, which led to clogging of the filter. Filter papers were transferred to a clean glass jar and shipped to the University of Toronto for analysis. Field duplicates were collected after the primary sample using the same method. Field blanks were collected by pumping 4 L of DI water through the system.

Quantifying microparticles: Manta samples

In the laboratory, each manta sample was first sieved through a 212-µm stainless steel sieve. This step was

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needed to remove excess water and small sediments. Afterwards, large nonplastic particles, such as leaves, feathers, and rocks, were rinsed into the sieve and removed. All remaining particles were rinsed into a clean jar using reverse osmosis (RO) water and examined under a dissection microscope. Anthropogenic particles (i.e., particles that appeared to be anthropogenic in origin such as microplastic, glass, or metal, or were dyed [e.g., blue cotton fiber]) were visually identified and extracted onto a large petri dish with double-sided sticky tape. Each extracted particle was characterized by its color and morphology (i.e., fiber, fragment, foam, film, pellet, sphere, fiber bundle; Rochman et al. 2019), measured, and photographed and the information recorded on a data sheet. Because we were interested only in comparisons of counts and morphologies between sample types for the present study, we did not include chemical identification results because doing so was unnecessary to meet our objectives. Spectroscopic analyses was performed on these samples for the objectives of the main study and are reported elsewhere (Sutton et al. 2019).

Quantifying microparticles: Grab samples

In the laboratory, each 1-L grab water sample was filtered using vacuum filtration through a 20-μm PC membrane filter in a clean cabinet. The PC filter was then transferred onto a clean glass petri dish and particles were evaluated under a dissection microscope using the same method employed for the manta samples, with 1 exception. For the 1-L grab samples, only 10 particles from each color and morphology were extracted onto a large petri dish with double-sided sticky tape for measurements and photographs; all remaining anthropogenic particles were recorded by morphology and color on the data sheet (i.e., photographs and measurements were not collected). Lastly, we photographed and measured the size of each particle that was extracted and mounted on tape.

Quantifying microparticles: Pump samples

Once received in the laboratory, pump filter samples were sonicated to release microparticles from the filters by placing each filter in a jar filled with RO water and then placing the jar into a sonicator, ensuring that the water level of the sonicator was above the water level in the jars. After sonicating samples for 60 min, the filters were rinsed with RO water into the clean jar and the sample filters were discarded. Next, density separation was performed to separate microplastics from denser nonplastic particles. Each sample was filtered and collected on a 25-μm stainless steel mesh sieve. Particles that remained on the sieve were transferred into a 500-mL separatory funnel filled with filtered 1.4 g/mL $CaCl_2$ solution and left overnight. After 24 h, the bottom layer in the separatory funnel was released and discarded. The remaining content in the separatory funnel was then separated into 6 size fractions by sieving the sample through 6 stacked stainless steel mesh sieves (1 mm, 500 μm, 355 μm, 125 μm, 45 μm, and 25 μm). Particles were rinsed off each of the sieves using RO water into a clean glass jar corresponding to the respective size fraction. The procedures for microparticle extraction and characterization in pump samples were the same as for the grab samples.

Quality assurance and quality control

Quality assurance and quality control procedures were implemented in the field as well as the laboratory. Field blanks and field duplicates were collected as described above (see *Sample collection* section). Field blanks were collected to assess the potential for microparticles to be introduced as a result of sample collection, transport, extraction and quantification. Field duplicate samples were taken immediately after the collection of the primary field sample to measure the sample variability.

To avoid cross-contaminating the field samples, rigorous field protocols were implemented (Sedlak et al. 2017) including avoiding synthetic textiles that might shed fibers, covering sampling equipment while not in use, minimizing exposure of sample to ambient air by covering sieves with foil and placing field samples and sieves into closed containers such as coolers, and avoiding using plastic tools and equipment where possible. We also analyzed 3 laboratory blanks of RO water per sample type to account for procedural contamination in the laboratory, taking each blank sample through the same process of extraction as the corresponding samples. In the laboratory, analysts wore cotton lab coats, minimized plastic use during sampling and analysis, ensured minimal exposure of samples to the air (e.g., working under a clean cabinet as much as possible and keeping samples covered whenever possible), and used clean glassware and tools (i.e., cleaned detergent and RO water before and after use).

To correct for procedural contamination in our samples, we subtracted from each sample type the average number of microparticles from each color–morphology combination (e.g., blue fragment, black fiber) observed within each of the respective laboratory and field blanks (Covernton et al. 2019).

RESULTS AND DISCUSSION

Informing QA/QC: Microparticles in field and laboratory blanks

Because microplastics are ubiquitous in air, water, and dust, blank samples must be taken to account for procedural contamination during sample collection and laboratory analysis. Field and laboratory blanks provide information about contamination during sampling and analysis that cannot be attributed to the sample. For the present case study, we examined results from 3 types of collection methods: manta, grab sampling, and in situ pump sampling (Table 1). In grab and manta samples, we generally observed more particles per liter in the field samples than in the field blanks for each color-morphology (Table 1). Manta samples, which sample the largest volume of water, had the largest signal-to-noise ratio, with particle counts in the field samples being much larger than in the blanks.

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Table 1. Field blank, laboratory blank and field sample microparticle counts of manta, grab, and pump by color-morphology[a]

Sampling method	Morphology	Fiber												Fragment							Fiber bundle		Film
	Color	Black	Dark blue	Blue	Light blue	Clear	White	Green	Red	Yellow	Pink	Grey	Gold	Black	Clear	Blue	White	Red	Yellow	Orange	Clear	White	Clear
Manta	FB #1	2	0	6	0	26	0	0	0	5	4	0	0	0	0	2	1	0	2	0	2	2	0
	FB #2	5	8	12	2	0	10	0	3	2	2	0	0	0	0	0	1	0	0	0	0	8	0
	FB avg	4	4	9	1	13	5	0	2	4	4	0	0	0	0	1	1	0	1	0	1	5	0
	LB #1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	LB #2	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	LB #3	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	LB average	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sum of averages	4	4	9	1	14	5	0	2	4	4	0	0	0	0	1	1	0	1	0	1	5	0
	Limit of detection	12	12	27	3	42	15	0	6	12	12	0	0	0	0	3	3	0	3	0	3	15	0
	Field sample range	2–452	0–460	2–523	0–102	0–160	0–65	0–47	0–122	0–3	0–137	0–98	0–1	0–95	1–399	0–41	0–231	0–7	0–12	0–6	0–14	0–18	0–20
Grab	FB #1	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	FB #2	2	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	FB average	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	LB #1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
	LB #2	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	LB #3	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	LB average	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sum of average	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Limit of detection	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Field sample range	0–2	0–3	0	0	0–3	0–1	0	0–1	0	0–1	0–2	0	0	0–1	0	0	0	0	0	0	0	0
Pump	FB	8	32	46	1	159	0	0	0	0	10	0	0	2	1	0	0	2	1	24	0	0	1
	Field sample	7	9	16	1	135	1	1	2	4	1	0	0	1	3	0	3	0	0	3	0	0	5

[a] Two field blanks (FBs) and 3 lab blanks (LBs) were taken for both manta and grab sampling methods. The total number of microplastics per color-morphology in each sample is listed, in addition to the average number (rounded to the nearest whole integer) across the FBs or LBs. We also include the sample limit of detection, which is calculated as 3× the average amount in the blanks. The field sample ranges show the microplastic counts by each color-morphology observed among the 9 field samples with respect to the sampling method (manta and grab). Only 1 FB and field sample were used for pump analysis due to the high amount of contamination, as shown in the FB.

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In contrast, we observed microparticle counts per liter that were sometimes larger in the pump field blank than the pump field samples, depending on the color and morphology. The exposure of water samples to contamination in the air while processing water through the pump attributed to the high level of microparticles observed (per liter) in field blanks. As a result, we eliminated pump sampling results from further consideration. To improve the pump method, a thorough examination of potential sources of procedural contamination is needed. In addition, more volume could be sampled to bring the signal above the noise. Overall, these results indicate that field blanks are necessary and should be assessed early to inform sampling procedures, including how a sample is collected and the volume sampled.

Some recent metaanalyses on quantifying microplastics in various matrices, including sediments (Hanvey et al. 2017), surface water (Erni-Cassola et al. 2019), and marine biota (Hermsen et al. 2018; Erni-Cassola et al. 2019), revealed that many studies did not adequately characterize procedural contamination. Hanvey et al. (2017) indicated that only 7 of 43 reviewed studies included some form of laboratory blanks and that none included field blanks to control for contamination introduced as a result of sample collection, transport, and analyses.

Indeed, laboratory blanks are a necessary approach to account for background contamination, including airborne fibers in the laboratory during sample preparation (Dris et al. 2017; Wang and Wang 2018). In more recent publications (i.e., after Hanvey et al. 2017), collection and analysis of laboratory blanks to account for contamination during analysis has become a more common practice for microplastic research. Field blanks, although common for environmental monitoring of chemical contaminants, are still rarely included in microplastic study designs. In the field, contamination may be introduced from a variety of sources, including sample collection equipment, clothing worn by field and laboratory staff, and air and dust present in the collection area, and may be more difficult to control. Our results indicate that sample values may be overestimated if field procedural contamination is not adequately assessed. Hence, we strongly recommend including field blanks (in addition to laboratory blanks) as standard practice for microplastics research.

Similar to methods employed for the analyses of chemical contaminants, we recommend establishing a method limit of detection for microplastic concentrations in field samples (see Bråte et al. 2018, for an example). Blank measurements allow us to measure the background microparticle concentration due to procedural contamination, and for microplastic analysis we suggest aiming for sampling in a manner that allows our ambient particle count to be 3× above the amount in the blank samples (i.e., signal-to-noise ratio of 3; Table 1), as is often used for chemical analysis (Shrivastava and Gupta 2011). The amount of procedural contamination can be assessed for each color–morphology combination, or even for each color–morphology–polymer type combination if spectroscopy is used for all particles. These particle classes can be thought of in the same way as different congeners within classes of chemicals, and concentrations in the blanks can be subtracted from the counts in the samples (Rochman et al. 2019).

Informing QA/QC: Field duplicates

In addition to laboratory and field blanks, the present study included field duplicates to measure the sample variation. Here, we show the concentrations of anthropogenic particles in pairs of primary and duplicate samples (2 from manta and 2 from grab) (Figure 2). Because the objective was to compare the content between 2 field duplicate samples, raw data were reported without correcting for the particles found in blanks. Moreover, because the mesh

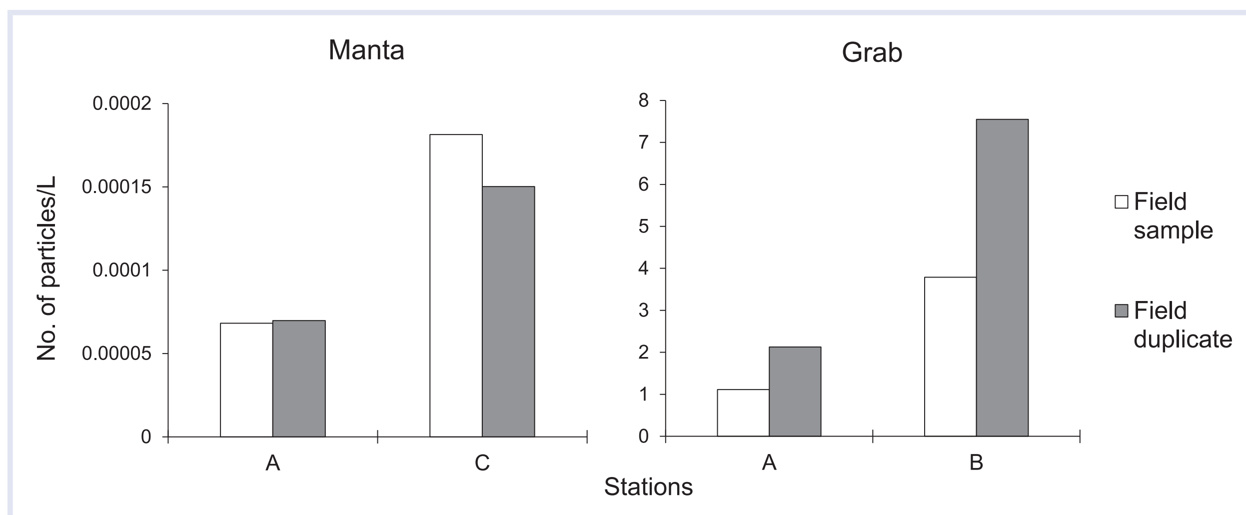

Figure 2. Microparticle concentrations in field samples and field duplicates. Comparison between manta (left) and grab (right) microplastic concentrations (note differences in *y*-axes). Values are not corrected for blank contamination. Each sampling station (A, B, or C) includes a paired field and duplicate sample. Because manta samples are not well suited to capture microfibers, the manta concentrations do not include fibers observed in the samples.

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Table 2. Percentage of relative standard deviation of microparticle concentration (particles per liter) between each paired field sample and field duplicate within the sampling station (A, B, or C), as shown in Figure 2[a]

Sampling station-method	Mean	Standard deviation	%RSD
A–Grab	1.62	0.717	44.2
B–Grab	5.67	2.66	46.9
A–Manta	6.89E–05	1.13E–06	1.63
C–Manta	0.000166	2.21E–05	13.3

[a] The table shows the percentage of relative standard deviation (%RSD) calculated by taking the standard deviation (SD) of a field and duplicate sample divided by the mean, times 100. The higher the %RSD, the higher the variability between the field sample and field duplicate of a sampling method. The manta values do not include contributions from fibers observed in the samples.

size of the manta nets do not adequately capture fibers, fiber particles in the manta samples were excluded.

The variability between the paired duplicates for the grab samples is greater than between duplicate manta samples (Table 2). For grab samples, both duplicate samples captured roughly double the concentration of microparticles observed in the primary samples. In contrast, for manta samples, the relative standard deviation between samples for both pairs of duplicates was less than 15% (Table 2). This implies that the small sample volume of the grab samples may magnify the variability observed. Thus, we suggest larger volume grab samples in the future. Using a larger sample volume would also increase the signal-to-noise ratio, thus improving the accuracy of estimates more broadly.

Based on the results of the present case study, we recommend the use of duplicate samples to assess sample variability, a standard practice in monitoring of chemical contaminants. For large-volume samples, duplicates may only be necessary at 5% of all sampling sites (Sutton et al. 2019). For smaller volume sampling, we might suggest duplicates or triplicates at all sample sites to account for the greater variability. According to Coverton et al. (2019), replication of small-volume samples (e.g., grab) can dampen the variability and predict microplastic abundance more accurately.

Sampling to match objectives: Microparticle quantification and characterization via different methodologies

In the present study, we sampled microplastics and other anthropogenic microparticles from surface waters using different collection methods. This allowed us to compare results and evaluate best practices for sampling, especially in light of the objective of the management questions to be answered or goals of monitoring program. The array of sizes, types (i.e., based on density), and morphologies of microparticles captured is highly dependent on the collection method employed. Thus, given the diversity of microplastics as a class of contaminants, the questions one is trying to answer need to be considered during design of a sampling program.

Net-tow sampling, such as with a manta trawl or neuston net, is widely used to study microplastics in surface waters because of its ability to capture microplastics from large volumes of water. The fact that these tools are not designed to adequately capture particles smaller than the given mesh size also simplifies the extraction process (Coverton et al. 2019). However, this becomes a limitation when we want to quantify and/or monitor small-sized fractions (<0.3 mm) of microplastics, or microfibers that are small in diameter. Small-volume discrete sampling, such as grab samples, allows us to detect a wider range of microplastics because all particles in the sample are retained (Barrows et al. 2017; Coverton et al. 2019). In Figure 3 below, we assessed 2 sampling methods, manta and grab, and compare the microparticle concentrations (particles/L) and characteristics between methodologies. Here, microfibers

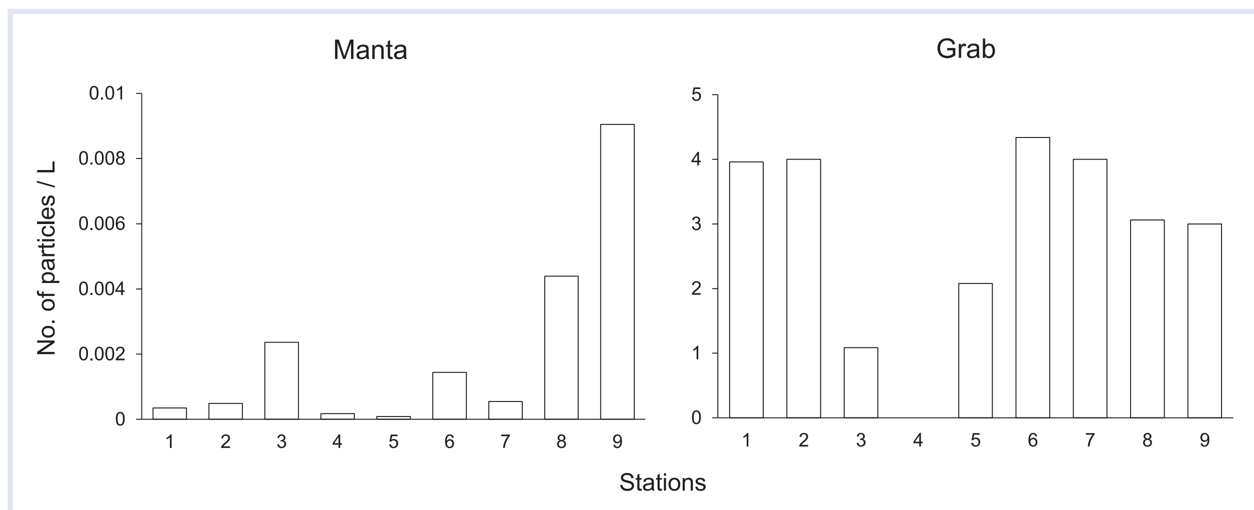

Figure 3. Number of microparticles sampled per liter across 9 stations. Comparison between manta (left) and grab (right). Note the scaling differences on the *y*-axes.

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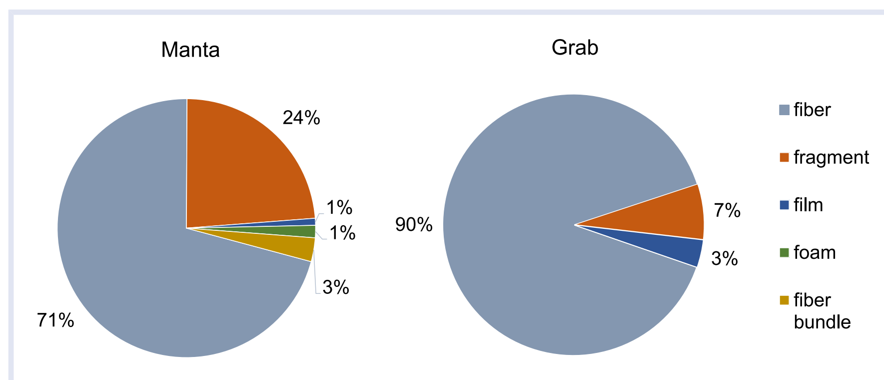

Figure 4. Morphology distribution of samples between sampling methods. Comparison between manta (left) and grab (right). Microparticle morphologies include fiber, fragment, film, foam, and fiber bundle.

were included in counts for both methodologies, and data were blank corrected.

With the exception of station 4, microparticles captured in grab samples were 2 to 3 orders of magnitude higher than in manta samples (Figure 3). This is consistent with results from Barrows et al. (2017) comparing neuston net sampling (similar to manta) to grab sampling. According to Coventon et al. (2019), microplastic concentration and mesh size are negatively correlated. Towed samples (e.g., manta or neuston net) result in lower microplastic concentrations than discrete samples (e.g., grab methodologies; Coverton et al. 2019). Although manta samples tend to capture some microfibers and other microplastics smaller than the given mesh size, counts will likely be an underestimation because small particles can escape (Barrows et al. 2017).

Aside from concentration, a greater number of morphologies and sizes of microparticles were detected in manta samples (Figures 4 and 5). For both methods, the most common morphology detected was fibers (Figure 4). Because grab samples collect microparticles from a smaller volume of water, only 3 morphologies of microparticles (i.e, fiber, fragment, and film) were found in grab samples. For manta, 5 morphologies (i.e., fiber, fragment, film, foam, and fiber bundle) of microparticles were found in all samples.

The morphology, or shape, of a particle can provide an important clue for deducing the potential sources of microplastics (Rochman et al. 2019). For instance, fibers are often attributed to synthetic textiles and thus are a common morphology observed in effluent samples taken from wastewater treatment plants due to discharges from washing machines (Browne et al. 2011; McCormick et al. 2014; Sutton et al. 2016; Dris et al. 2017). Foam is likely expanded polystyrene from single-use packaging (Browne et al. 2011; McCormick et al. 2014; Rochman et al. 2019), and thus these particles are often found as litter on beaches. Thus, if monitoring is conducted to inform identification of sources of contamination, the sampling methodologies should be carefully considered. Our results suggest grab sampling may be most effective for quantifying microfibers

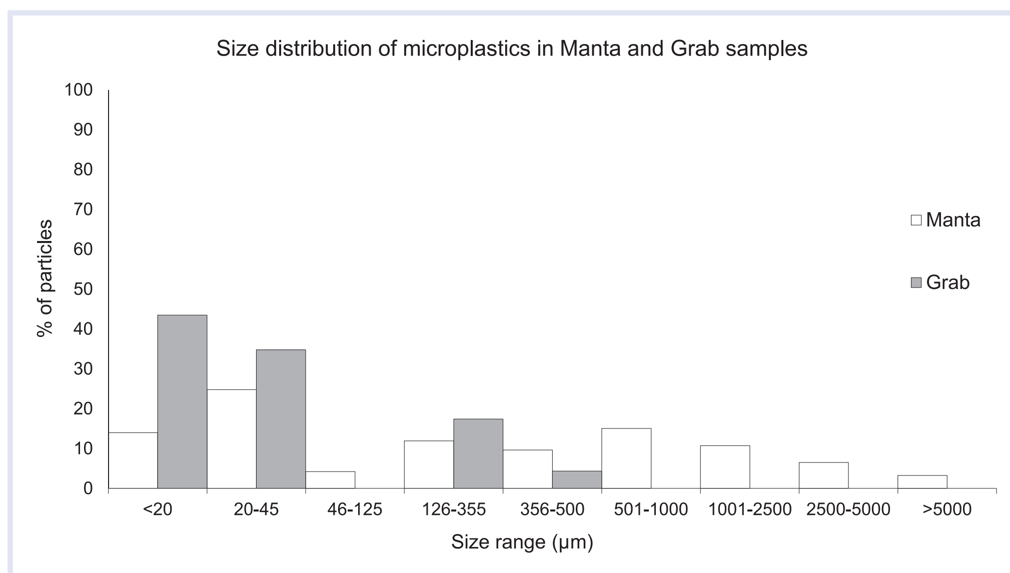

Figure 5. Bar graph showing the size distributions of microparticles in manta (white) and grab (grey) samples. Size distributions of each sample type are blank corrected.

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in surface waters, whereas manta trawls may be best to characterize diverse morphologies.

In addition to morphology, the size and length of microparticles collected differed among sampling methodologies (Figure 5). Here, we measured the size of the microparticles in their smallest dimension to allow for comparison of what was captured by the sampling methodology. Although it is a common practice in microplastics research to report fiber lengths (Coverton et al. 2019), measuring the widths offered insights to the minimum fiber size retained by sampling.

For grab samples, the majority of the anthropogenic particles characterized were <45 μm in their smallest dimension, and we found that the number of microparticles generally decreased in a stepwise fashion as the size fraction increased. Manta samples, as expected, captured an overall higher number of microparticles in size fractions larger than 355 μm (45.1% of all particles for manta and 4.35% for grab), due to the size of the mesh used to process the manta samples and the fact that manta trawls sample a much larger quantity of water in comparison to grab. Still, there was no clear pattern regarding the size of particles captured when using a manta trawl. Interestingly, the size fraction with the highest microparticle distribution, 20 to 45 μm, was still much smaller than the mesh. This size fraction was made up of some thin, long fibers, likely retained in the mesh due to horizontal orientation, and some nonfibrous particles that were likely stuck to the mesh or caught up in the natural organic material in the net during sampling (Coverton et al. 2019). Capture of these particles is likely by random chance and is expected to be an underestimate of the total number of these small-sized particles. For this reason, the quantities of particles with dimension smaller than the mesh size should be treated with caution and considered qualitative estimates.

In general, when selecting the appropriate sampling methodologies for microplastic research, we must consider the particle size range that is of interest, and make sure the chosen method accurately samples it. Multiple methods may be used to provide complementary data on a wider range of sizes and morphologies.

Implications for monitoring and ecological risk assessment

Long-term microplastics monitoring programs are useful to inform management strategies. Whether it is to understand the sources and distribution, or to establish policies to reduce emissions or the efficacy of these policies, we need to select appropriate sampling methods with harmonized procedures that will assure quality measurements. These must include careful attention to QA/QC.

In addition, quantification and characterization of microplastics in the environment is necessary to better characterize the potential risks associated (Syberg et al. 2015). Exposure to microplastics can be harmful to marine life (Teuten et al. 2009; Rochman et al. 2013; Wright et al. 2013). To gain a better understanding of the effects of microplastics on marine life, we need to perform risk assessments. To do so, we must select the correct sampling method to ensure accurate measurement of the level and type of exposure specific to the species of interest. For example, the dominant zooplankton in SF Bay are *Acartia* species with a diet consisting of particles <200 μm (Rollwagen Bollens and Penry 2003). In contrast, Northern anchovy (*Engraulis mordax*) observed in SF Bay are small planktivorous fish that feed on 0.65- to 3.7-mm prey (Leong and O'Connell 1969; O'Connell 1972). Thus, copepods and anchovies ingest different sizes of microplastics due to distinct gape size limits. Therefore, if the goal is to quantify microplastics exposure to both animals in SF Bay, we must combine both manta and grab sampling methods to provide relevant information for risk assessment.

CONCLUSION

Our study confirms the importance of choosing the appropriate sampling methods for quantifying microplastics, as well as the importance of QA/QC for measuring procedural contamination and variability. Manta sample collection, although widely used, underestimates small-sized microplastics. Manta sampling may be preferred for measuring microplastics exposure for larger animals with gape size no smaller than the mesh size. It may also be preferred if the goal is to capture a diversity of morphologies in a larger size range to inform source identification.

However, many marine invertebrates and fish consume smaller particles, which may not be accurately captured through manta sampling. Grab sampling is generally considered best for quantifying microfibers and other small particles. For any sampling, the sample volume collected is an important consideration in the monitoring design. Small-volume samples such as grab samples tend to show greater variability between duplicate samples than do large-volume samples. Thus, including duplicate samples at all sampling sites will increase the accuracy of estimation. Larger volumes may also reduce the signal-to-noise ratio between a field sample and a blank.

Field and laboratory blank samples should be included as a standardized practice for quantifying microplastics to ensure procedural contamination does not result in overestimation of concentrations in the environment. A microplastic monitoring or sampling plan that includes appropriate sampling methods with robust QA/QC practices can provide reliable microplastics information to help answer management questions related to mitigation and inform ecological risk assessment.

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Data Availability Statement—All data are available in the Supplemental Data.

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SUPPLEMENTAL DATA

An Excel workbook contains all the raw data.

REFERENCES

Barrows A, Neumann C, Berger M, Shaw S. 2017. Grab vs. neuston tow net: A microplastic sampling performance comparison and possible advances in the field. *Anal Methods* 9(9):1446–1453. https://doi.org/10.1039/c6ay02387h

Bråte ILN, Hurley R, Iversen K, Beyer J, Thomas KV, Steindal CC, Green NW, Olsen M, Lusher A. 2018. Mytilus spp. as sentinels for monitoring microplastic pollution in Norwegian coastal waters: A qualitative and quantitative study. *Environ Poll* 243:383–393.

Browne MA, Crump P, Niven SJ, Teuten E, Tonkin A, Galloway T, Thompson R. 2011. Accumulation of microplastic on shorelines woldwide: Sources and sinks. *Environ Sci Technol* 45(21):9175–9179. https://doi.org/10.1021/es201811s

Bucci K, Tulio M, Rochman CM. 2020. What is known and unknown about the effects of plastic pollution: A meta-analysis and systematic review. *Ecol Appl* 30(2):e02044.

Chae Y, An Y. 2017. Effects of micro- and nanoplastics on aquatic ecosystems: Current research trends and perspectives. *Mar Pollut Bull* 124(2):624–632. https://doi.org/10.1016/j.marpolbul.2017.01.070

Cole M, Lindeque P, Halsband C, Galloway TS. 2011. Microplastics as contaminants in the marine environment: A review. *Mar Pollut Bull* 62(12): 2588–2597. https://doi.org/10.1016/j.marpolbul.2011.09.025

Covernton GA, Pearce CM, Gurney-Smith HJ, Chastain SG, Ross PS, Dower JF, Dudas SE. 2019. Size and shape matter: A preliminary analysis of microplastic sampling technique in seawater studies with implications for ecological risk assessment. *Sci Total Environ* 667:124–132. https://doi.org/10.1016/j.scitotenv.2019.02.346

Dris R, Gasperi J, Mirande C, Mandin C, Guerrouache M, Langlois V, Tassin B. 2017. A first overview of textile fibers, including microplastics, in indoor and outdoor environments. *Environ Pollut* 221:453–458. https://doi.org/10.1016/j.envpol.2016.12.013

Erni-Cassola G, Zadjelovic V, Gibson MI, Christie-Oleza JA. 2019. Distribution of plastic polymer types in the marine environment. A meta-analysis. *J Hazard Mater* 369(February):691–698. https://doi.org/10.1016/j.jhazmat.2019.02.067

[GESAMP] Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection. 2015. Sources, fate and effects of microplastics in the marine environment: A global assessment. In: Kershaw PJ, editor. London (UK): IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP. GESAMP 90. p 19–36.

[GESAMP] Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection. 2019. Guidelines or the monitoring and assessment of plastic litter and microplastics in the ocean. In: Kershaw PJ, Turra A, Galgani F, editors. IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP/ISA. GESAMP 99. 130 p.

Hanvey JS, Lewis PJ, Lavers JL, Crosbie ND, De KP, Clarke BO, Pete PET. 2017. A review of analytical techniques for quantifying microplastics in sediments. *Anal Methods* 9(9):1369–1383. https://doi.org/10.1039/c6ay02707e

Helm PA. 2017. Improving microplastics source apportionment: A role for microplastic morphology and taxonomy? *Anal Methods* 9(9):1328–1331. https://doi.org/10.1039/c7ay90016c

Hermsen E, Mintenig SM, Besseling E, Koelmans AA. 2018. Quality criteria for the analysis of miroplastic in biota samples: A critical review. *Environ Sci Technol* 52:10230–10240. https://doi.org/10.1021/acs.est.8b01611

Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, Narayan R, Law KL. 2015. Plastic waste inputs from land into the ocean. *Science* 347(6223):768–771.

Leong RJH, O'Connell CP. 1969. A laboratory study of particulate and filter feeding of the northern anchovy (*Engraulis mordax*). *J Fish Res Board Can* 26(3):557–582. https://doi.org/10.1139/f69-053

McCormick A, Hoellein TJ, Mason SA, Schluep J, Kelly JJ. 2014. Microplastic is an abundant and distinct microbial habitat in an urban river. *Environ Sci Technol* 48(20):11863–11871. https://doi.org/10.1021/es503610r

O'Connell CP. 1972. The interrelation of biting and filtering in the feeding activity of the northern anchovy (*Engraulis mordax*). *J Fish Res Board Can* 29:285–293. https://doi.org/10.1139/f72-047

Rochman CM, Brookson C, Bikker J, Djuric N, Earn A, Bucci K, Athey S, Huntington A, Mcilwraith H, Munno K et al. 2019. Rethinking microplastics as a diverse contaminant suite. *Environ Toxicol Chem* 38(4): 703–711. https://doi.org/10.1002/etc.4371

Rochman CM, Cook A-M, Koelmans AA. 2016. Plastic debris and policy: Using current scientific understanding to invoke positive change. *Environ Toxicol Chem* 35(7):1617–1626. https://doi.org/10.1002/etc.3408

Rochman CM, Hoh E, Hentschel BT, Kaye S. 2013. Long-term field measurement of sorption of organic contaminants to five types of plasticpellets: Implications for plastic marine debris. *Environ Sci Technol* 47(3):1646–1654. https://doi.org/10.1021/es303700s

Rollwagen Bollens GC, Penry DL. 2003. Feeding dynamics of *Acartia* spp. copepods in a large, temperate estuary (San Francisco Bay, CA). *Mar Ecol Prog Ser* 257:139–158. https://doi.org/10.3354/meps257139

Sedlak M, Sutton R, Box C, Sun J, Lin D. 2017. Sampling and analysis plan for microplastic monitoring in San Francisco Bay and adjacent national marine sanctuaries FINAL. Richmond (CA): San Franciosco Estuary Institute. 136 p.

[SFEI] San Franciosco Estuary Institute. 2017. The pulse of the bay: The 25th anniversary of the RMP. Richmond (CA). 96 p.

Shrivastava A, Gupta BV. 2011. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chron Young Sci* 2(1):21–25.

Sutton R, Lin D, Sedlak M, Box C, Gilbreath A, Holleman R, Miller L, Wong A, Munno K, Zhu X et al. 2019. Understanding microplastic levels, pathways, and transport in the San Francisco Bay region. Richmond (CA): San Francisco Estuary Institute. SFEI Contribution No. 950. 389 p.

Sutton R, Mason SA, Stanek SK, Willis-Norton E, Wren IF, Box C. 2016. Microplastic contamination in the San Francisco Bay, California, USA. *Mar Pollut Bull* 109(1):230–235. https://doi.org/10.1016/j.marpolbul.2016.05.077

Syberg K, Khan FR, Selck H, Palmqvist A, Banta GT, Daley J, Sano L, Duhaime MB. 2015. Microplastics: Addressing ecological risk through lessons learned. *Environ Toxicol Chem* 34:945–953. https://doi.org/10.1002/etc.2914

Teuten EL, Saquing JM, Knappe DRU, Barlaz MA, Jonsson S, Björn A, Rowland SJ, Thompson RC, Galloway TS, Yamashita R et al. 2009. Transport and release of chemicals from plastics to the environment and to wildlife. *Philos Trans R Soc B Biol Sci* 364(1526):2027–2045. https://doi.org/10.1098/rstb.2008.0284

Thompson R. 2015. Microplastics in the marine environment: Sources, consequences and solutions. *Mar Anthropog Litter* 185–200. https://doi.org/10.1007/978-3-319-16510-3

Wang W, Wang J. 2018. Trends in analytical chemistry investigation of microplastics in aquatic environments: An overview of the methods used, from field sampling to laboratory analysis. *Trends Anal Chem* 108:195–202. https://doi.org/10.1016/j.trac.2018.08.026

Wright SL, Thompson RC, Galloway TS. 2013. The physical impacts of microplastics on marine organisms: A review. *Environ Pollut* 178:483–492. https://doi.org/10.1016/j.envpol.2013.02.031

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